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Synthetic raw materials - possibility to increase refractory materials resistance

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Abstract. The analysis of refractory materials and factors groups destruction types causing these destructions during operation of refractory materials is presented. One of the reasons preventing further increase of refractory resistance is shown to be natural barrier of impurities presence in natural raw materials for refractory production. Disclosed is a method for natural and/or man-made raw materials deeper enrichment by hydrochemical processing methods. This work is devoted to the chemical synthesis of raw materials enrichment for the production of refractory materials with increased resistance. The studies were carried out with the aim of developing a technology for producing high-purity aluminum powders with high physical and mechanical properties using raw materials from the Ural field and metakaolinite to produce high-purity alumina from aluminum sulfate. Thus, the authors tested the technology of complex processing of industrial and/or natural aluminosilicate materials waste using an extractable leaching solution of sulfuric acid - an ammonium hydrosulfate solution.

1. Introduction

The refractory materials production technology always develops together with the technologies' development of metallurgical processes. The refractories and lining quality is determined, and in turn determines the performance and efficiency of the thermal metallurgical units. Increasing requirements for metallurgical processes, both in terms of production intensity and metal quality, leads to increasing requirements for refractory materials and linings resistance in general [1–3], which are estimated by reducing the refractory per unit specific consumption of produced product.

Depending on the phase-structural conversion nature occurring during refractory operation in different environment and conditions, eight types of wear and tear are established:

1) high-temperature chemical corrosion;
2) thermal chipping;
3) structural strength loss (regeneration or 'aging' of the refractory);
4) melting;
5) pyroplastic deformation;
6) molten erosion;
7) gas phase sublimation and erosion;
8) mechanical destruction.

The first two types account for 80–90 % of refractory linings failure cases. In reality, there is usually simultaneous exposure to several types of wear and tear. The above phase-structural transformations type and intensity of the refractory during thermal aggregate linings operation are influenced by a large number of factors:

1) chemical and phase compliance of refractory is against an aggressive factor (melt, gas fluid composition, dust);

2) compliance of refractory structure with operating conditions (by density and strength, by gas permeability and melt permeability, heat conductivity and heat resistance);

3) compliance with the thermal unit standard operating mode;

4) refractory material thermal energy density (characterizes energy density in one cm^3 of crystalline phase taking into account its melting temperature, $(kJ \times deg)/cm^3$);

5) impurities composition and quantity in the refractory forming with aggressive chemical factor low-melting compounds and melts with low viscosity at the thermal unit working temperatures.

Compliance of the refractory material/product with some of these factors is established at the lining design and refractory type and appearance selection stages (1 and 2 factors); Impact of operating conditions (3 factors) depends only on the technological discipline of consumer. Thermal energy density is a complex indicator depending on the selected refractory phase type (such as chemical bonding, the crystal lattice parameters), the material and product obtaining method. The impurities composition and amount in the refractory depends on the raw material used (natural or synthetic) and producing method of the material and product (introduced in receiving process of the functional additives and the lighter/more fusible components removing possibility in the refractory production process).

If the first 4 factors are quite easily regulated and/or set during technological processes preparation and implementation in metallurgy and refractory products production and, theoretically, can be indefinitely improved as science develops, and the empirical observations mass increases, the 5th factor has a natural and quite obvious limit of development, to which practically all producers of refractory products have now approached. This is very well visible on the nomenclature of the main periclase and periclasocarbon refractory for black metallurgy: GOST 28874–2004 (reprinting GOST 28874–90) "Refractory. Classification" refers to periclase all refractory materials containing 85 % by weight MgO inclusive. According to GOST 4689–94 "Periclase refractory. Specification", content MgO of the refractory starts with 89 wt. %. As early as 5 years ago periclase and/or periclase carbon products with a content of 95 wt % MgO were considered qualitative. Now we use brand 97 periclase (97.0–97.5 wt. % MgO), also we speak about brand 98 desirability, and 99 [4–7] is better. But there is no natural raw material of this quality, given the basic genesis type of the magnesia raw material in nature (calcium carbonates into magnesium carbonates recrystallization in seawater) any magnesia raw material will necessarily contain some calcium ions in the solid solution in the magnesia lattice. And it is impossible to get rid of them by any mechanical and/or pyrotechnic enrichment methods. The same applies to iron (II) oxide forming solid solutions with magnesium oxide and, more broadly, to any natural raw material.

Thus, the chemical enrichment of natural and/or chemical synthesis of artificial raw materials for the production of refractory materials with increased resistance is now becoming increasingly apparent and relevant. And such examples already exist, namely, continuing a magnesian raw materials subject: a number of producers receives natural brines processing (sea water, natural bischofites) magnesium oxide with purity to 99.99 wt. % MgO (magnesia burned) for the chemical, electrometallurgical, electronic, ceramic industries, medicine. The main magnesium oxide producers from seawater are the USA, Netherlands, Japan, Mexico, Israel, Ireland, Jordan [8, 9]. And, although at present this technology cost is quite high, the hydrochemical enrichment or this technology (synthetic) production direction of basic refractory oxides (MgO, Al_2O_3, ZrO_2, Cr_2O_3) as well as carbon is seen as the only refractory materials increasing the chemical purity prospect. In addition, the hydrochemical method of enriching/producing pure refractory materials enables:

- still at the production stage cheaply and controllably alloy their structures, obtaining the required physical and chemical properties;
- involve in the clean materials production not only natural quality raw materials, but also technogenic wastes, simultaneously solving tasks of resource saving and anthropogenic impact reduction on the environment.

2. Materials and method

The authors have tested the technology of complex processing of industrial and/or natural aluminosilicate materials production wastes with the use of recoverable leaching sulphuric acid solution - ammonium hydrosulfate solution. The technology includes:

1) Sulphuric acid leaching of raw materials with ammonium hydrosulphate solution with extraction of iron III and aluminum into the solution by the following reactions:

$$2AlOOH + 6NH_4HSO_4 = Al_2(SO_4)_3 + 3(NH_4)2SO_4 + 4H_2O\ Fe_2O_3 + 6NH_4HSO_4 =$$

$$= Fe_2(SO_4)_3 + 3(NH_4)2SO_4 + 3H_2O;$$

2) Filtration of acid-resistant residue containing RO_2, R_2O_5 oxides for subsequent use as raw materials for the production of building materials, refractories, ceramics, abrasives, etc;

3) Iron III deposition from ammonia solution and separation of iron hydroxide III for further use in the production of pigments;

4) Aluminium precipitation from ammonia solution and separation of aluminium hydroxide for further use as a raw material;

5) Obtaining a pure solution of ammonium sulfate from which crystalline ammonium sulfate is extracted; according to the technology developed and tested at the pilot plant, it is thermally decomposed into ammonium hydrosulfate and ammonia by reaction:

$$(NH_4)2SO_4 = NH_4HSO_4 + NH_3 \uparrow.$$

6) Return of the obtained ammonium sulfate and ammonia into production.

The raw materials for the study were selected as kaolin waste from the Zhuravlinny Log field (Plast, Chelyabinsk Region) and Poletaevskoye field (Chelyabinsk) as raw kaolin. Phase composition of initial materials includes, wt. %: kaolinite $Al_4[Si_4O_{10}](OH)_8$ – 95.0–97.0; quartz SiO_2 – 1.0–2.0 and feldspars (microcline K, $Na(AlSi_3O_8)$) – 1.0–3.0.

The offered technology of hydrochemical processing, allowing to improve opening of initial raw materials and to increase the target product yield, consists of:

- Preliminary grinding of raw materials up to the full passage through the sieve 0.08 mm;
- Preparation of H_2SO_4 technical solution with content: 10, 15 и 20 %;
- Pelletizing of ground raw materials with addition of H_2SO_4 solution;
- Classification of the obtained granules with the separation of the fraction of 3–7 mm and the return of the remaining fractions to the stage of granulation;
- Heat treatment of the obtained granules at a temperature of 350–600 °C.

Phase composition of granulated products after heat treatment at 350 (and 600) °C is presented, wt. %: metakaolinite $Al_2O_3{\cdot}2SiO_2$ – 85.0–94.0 (14.0-66.0); quartz SiO_2 – 1.0–2.0 (13.0–33.0); hydroslides $Na,K,Al_2[AlSi_3O_{10}](OH)_2$ – 3.0–14.0 (43.0–58.0) and aluminum sulfate 0.0–2.0 (15.0–23.0). It has been established that in the process of heat treatment the materials granulated with 20 % sulphuric acid solution and heat-treated at the temperature of not less than 500 °C are subject to the greatest change; at the same time the products have a latent-crystalline, almost amorphous structure of metakaolinite $Al_2O_3{\cdot}2SiO_2$. The leaching process of the target products is based on the reaction:

$$Al_2O_3\,2SiO_2 + 3H_2SO_4 = Al_2(SO_4)_3 + 2SiO_2 + H_2O \quad (1)$$

in slow boiling mode (5–7 min) and natural cooling of the solution (50–60 min) with further decantation and washing of the sludge. Wash water is collected and directed to obtaining a leaching solution. The results of the leaching process are presented in Table 1.

Table 1. Leaching process results.

Point No.			1	2	3	4	5	6
Process			Leaching					
Reagents, g	Metakaolinite	10 % H_2SO_4	3	–	3		–	
		15 % H_2SO_4	–	3	–	300	450	500
	25 % H_2SO_4 solution			17.5		1748	1966	2185
Conditions	Boiling point, °C			–			90	
	Boiling point, min		50	90		50	60	90
	Excess solution H_2SO_4, %				10 %			
	Δ Drying Point, °C		207	212	258	212	306	297
	Drying Point, min		40	71	110	71	104	120
Filter method			Decantation					
Mass of settled waters (master batch), g			375.6	308,9	301	1137	1949	3818
Mass of undissolved sediment, g		Practical	1.63	1.73	1.77	481	335	303
		Theoretical	1.62	1.62	1.62	270	270	270
Product yield (sludge), %			109	116	110	178	124	112
Additionally		pH initial/final	0.02/ 0.51	0.25/ 0.63	/0.75	/1.06	/0.94	/1.39

Based on the results of leaching, it can be concluded that the best way to achieve leaching is to use 15 % H_2SO_4 as the leaching agent.

The process of deposition of aluminum sulphate solution purified from iron oxides was performed at the temperature of solution 20–60 °C by step-by-step introduction of solution NH_4OH in the ratio 1 : 2 with pH control of the solution every 5–10 minutes to the final pH of the solution 4.0 – Table 2. After sedimentation the sludge settling, decantation and washing is performed. Drying and thermal treatment of hydroxide was carried out in laboratory furnaces at the temperature of 400–550 °C until the mass loss was stopped. The obtained product contains, wt. %: Al_2O_3 – 99.2; R_2O – 0.14; RO – 0.01; Fe_2O_3 – 0.05; SiO_2 – 0.08. The specific surface of the material was 5680 m^2/g, the average particle size was 2.7 μm.

Table 2. Precipitation results.

	Point No.	1	2	3	4	5	6	7	8
Reagents, g	$Al_2(SO4)_3$ solution	588	250	500	500			100	
	NH_4OH solution	–	146	268	278	431	548	915	670
	10 % solution of NH_4NaSO_3	520	520	1040	1210	2420	2420	1815	1815
Excess 10% solution of NH_4NaSO_3		1.5				2		1.5	
Boiling point, °C					82			74	
Boiling point, min					120				
Δ Drying Point, °C		127–278	162–347	166–296	204–343	194–289	193–320	201–315	199–321
Drying Point, min		124	235	189	180	199	201	200	198
Filter method					Decantation				
Product					$Al(OH)_3$				
Undissolved sediment mass (master batch), g		–	680	–	–	–	–	–	–
Sludge mass actual, g		14	13	33	41	38	140		
Sludge mass theoretical, g		13	13	26	26	26	52		
Product yield, %		108	100	127	158	146	269		
pH after adding technical ammonia		–	4.15	4	–	–	–	–	3.7
pH master batch		–	5.66	–	–	–	–	4.01	–

3. Conclusion

The possibility of developing a technology based on the raw materials of the Ural field using metakaolinite to produce pure aluminium oxide and other products from aluminium sulphate, which will make it possible to create an energy- and resource-efficient technology to produce high-purity Al_2O_3 powders with high level of physical and mechanical properties, was demonstrated.

References

[1] Baask A, Dyubers D et al 2011 *Ferrous metals* vol **9** pp 32–39
[2] Smirnov A N 2014 Main trends in the development of the market of refractory materials [an electronic resource] access mode: http://steellab.com.ua/news/2014/01/01.php
[3] Axelrod L M 2017 *New refractory* vol **11** pp 3–13
[4] Visloguzova É A, Kashcheev I D et al 2013 *Refractories and Industrial Ceramics* vol **2** pp 83-87
[5] Goto K, Hanagari S et al 2013 Progress and Perspective of Refractory Technology *Nippon steel technical report* vol **104** pp 21–25
[6] Poirier J 2015 *Metall. Res. Technol* vol **4** p 20
[7] Smirnov A N 2014 Main trends in the development of the market of refractory materials access mode: http://steellab.com.ua/news/2014/01/01.php
[8] Shand M A 2006 *The chemistry and technology of magnesia (*John Wiley&Sons Inc) p 263
[9] Kramer D A *Minerals Year Book 2002 Magnesium Compounds*. (USGS, Reston. Virginia)
[10] Kashcheev I D, Zemlyanoi K G et al 2014 *New refractory* vol **4** pp 6–13
[11] Kashcheev I D and Zemlyanoi K G et al 2010 *New refractory* vol **10** pp 28–35
[12] Zemlyanoi K G and Stepanova K O 2017 *New refractory* vol **10** pp 31–37